

The Crystal and Molecular Structure of 3,4-Dimethyl-6-phenyl-5,6-diaza-1,6a-dithiapentalene

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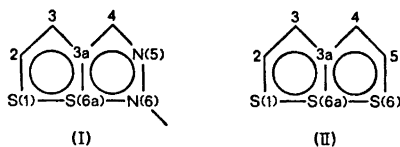
The title compound crystallizes in the monoclinic space group $P2_1/c$ with $Z=4$ and with unit cell dimensions, $a=12.778(2)$, $b=12.172(2)$, $c=7.875(3)$ Å, and $\beta=104.10(2)^\circ$.

X-Ray intensity data were collected on a Siemens AED diffractometer using $\text{MoK}\alpha$ radiation, and the structure was solved by Patterson methods and refined by full matrix least squares.

The molecule is almost planar with the methyl groups in eclipsed orientation, the H–H distances are 2.25(5) Å.

The bond lengths in the central ring system are: $\text{S}(1)–\text{S}(6a)=2.493(1)$ and $\text{S}(6a)–\text{N}(6)=1.779(2)$ Å with the angle $\text{S}(1)–\text{S}(6a)–\text{N}(6)=174.37(5)^\circ$, $\text{S}(1)–\text{C}(2)=1.681(2)$, $\text{S}(6a)–\text{C}(3a)=1.742(2)$, $\text{N}(6)–\text{N}(5)=1.324(2)$, $\text{C}(2)–\text{C}(3)=1.370(2)$, $\text{C}(3)–\text{C}(3a)=1.418(2)$, $\text{C}(3a)–\text{C}(4)=1.416(2)$, and $\text{C}(4)–\text{N}(5)=1.321(2)$ Å. Corrections for rigid body libration have been applied.

It has been shown through the structure analysis of 2-*t*-butyl-6-phenyl-5,6-diaza-1,6a-dithiapentalene¹ that the 5,6-diaza-1,6a-dithiapentalene system (I) is analogous to the 6a-thiathiophene system (II).²



The lengths of the S–S bonds in 6a-thiathiophenes are influenced by substituents,^{3,4} and the effect of methyl and phenyl groups on the S–S bonding have been found to agree with the results from CNDO/2 calculations.⁵

The degree to which substituents might affect the S–S–N bonding in I was thought to be of

interest, and the present structure study was therefore carried out.

STRUCTURE ANALYSIS

A sample of the title compound was generously supplied by D. H. Reid.^{6,7} The crystals are red needles elongated along *c*.

Crystal data $\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2$, M.W = 248.37. Monoclinic, space group $P2_1/c$ with $Z=4$ $a=12.778(2)$ Å, $b=12.172(2)$ Å, $c=7.875(3)$ Å, $\beta=104.10(2)^\circ$ $V=1187.9$ Å³ $D_x=1.389$ g/cm³, $D_m=1.385$ g/cm³ $\mu_{\text{MoK}\alpha}=4.10$ cm⁻¹

Unit cell dimensions and intensity data were measured on a paper-tape controlled Siemens AED diffractometer using $\text{MoK}\alpha$ radiation.

The cell dimensions quoted above are the results of a least squares treatment of the 20 values of 18 high order reflections measured at 20 °C.

The intensities of 2789 independent reflections within $\theta=28^\circ$ were measured by means of the five-value scan technique.^{4,8} 2154 of these with intensities greater than $2\sigma(I)$ were regarded as observed. The crystal used for intensity data collection had the dimensions 0.15 mm × 0.3 mm × 0.4 mm in the axial directions.

Corrections for Lorentz and polarization effects were carried out but absorption corrections were considered unnecessary.

Scattering factors for sulfur, nitrogen and carbon were taken from the *International*

Table 1. Atomic coordinates in fractions of corresponding cell edges. The numerical values of the standard deviations in parentheses are chosen to be in the range 3–30.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
S(1)	0.33816(4)	0.02325(4)	0.41899(8)
S(6a)	0.21398(4)	0.17385(4)	0.38069(7)
N(6)	0.13512(11)	0.29047(11)	0.35668(21)
N(5)	0.17992(12)	0.38725(12)	0.36696(22)
C(4)	0.27719(14)	0.37539(14)	0.39481(25)
C(3a)	0.31265(12)	0.26631(14)	0.40714(23)
C(3)	0.41163(13)	0.22896(15)	0.43753(25)
C(2)	0.42826(16)	0.11817(17)	0.44493(29)
C(7)	0.49921(18)	0.30650(22)	0.4622(4)
C(8)	0.33809(22)	0.47978(19)	0.4052(4)
C(9)	0.03116(14)	0.28396(15)	0.32457(26)
C(10)	-0.02495(19)	0.37788(21)	0.3061(4)
C(11)	-0.12560(20)	0.36918(26)	0.2725(4)
C(12)	-0.17217(18)	0.26947(25)	0.2608(4)
C(13)	-0.11705(19)	0.17694(25)	0.2804(4)
C(14)	-0.01552(17)	0.18325(20)	0.3128(4)
H(2)	0.4911(15)	0.0964(16)	0.465(3)
H(10)	0.0092(20)	0.4460(22)	0.312(4)
H(11)	-0.1669(21)	0.4322(24)	0.267(4)
H(12)	-0.2453(18)	0.2652(19)	0.233(3)
H(13)	-0.1484(19)	0.1093(21)	0.275(3)
H(14)	0.0211(19)	0.1224(20)	0.325(3)
H(7,1)	0.4719(19)	0.3608(22)	0.564(3)
H(7,2)	0.5551(16)	0.2634(17)	0.4905(28)
H(7,3)	0.5281(18)	0.3481(18)	0.356(3)
H(8,1)	0.4141(22)	0.4799(20)	0.312(4)
H(8,2)	0.3007(17)	0.5354(19)	0.3854(29)
H(8,3)	0.3522(16)	0.4869(17)	0.5205(29)

Tables,⁹ and the scattering factor curve used for hydrogen was taken from a paper of Stewart *et al.*¹⁰

The structure was solved by the heavy-atom (S) method, and the hydrogen positions were found from difference maps. The atomic parameters were refined by full matrix least squares (see Ref. 11) to an *R* of 0.033.

Final atomic coordinates and temperature parameters are given in Tables 1 and 2. The final structure factor list is available on request.

Rigid body analyses for various parts of the molecule have been carried out according to the method of Schomaker and Trueblood.¹² The parts treated in this way are:

1. The atoms of the fused five-membered rings plus C(7), C(8) and C(9).
2. The phenyl carbons plus N(6).

The corresponding librational tensors L_1 and L_2 are given in Table 3. One sees from the values there that the libration of the phenyl group, L_2 , is more pronounced than the libration of the other part. The eigenvector of L_2 corresponding to the largest libration, 10.9°, is directed roughly along N(6)–C(9)–C(12). The effect of this individual libration of the phenyl group on the “observed” bond lengths is discussed below.

Table 2. Temperature parameters U_{ij} (Å²) for sulfur, nitrogen and carbon, and U (Å²) for hydrogen. The expressions used are $\exp\{-2\pi^2(h^2a^*U_{11} + \dots + 2hka^*b^*U_{12} + \dots)\}$ and $\exp\{-8\pi^2U(\sin^2\theta/\lambda^2)\}$. The numerical value of the standard deviations in parentheses are chosen to be in the range 3–30. The U_{ij} 's and the U 's are multiplied by 10⁴ and 10⁵, respectively.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
S(1)	643(3)	463(3)	73(5)	59(3)	-7(3)	-336(3)
S(6a)	455(3)	410(3)	602(3)	-9(3)	-7(3)	-169(3)
N(6)	499(9)	421(8)	666(12)	19(7)	-6(8)	-200(8)
N(5)	604(10)	406(8)	705(12)	-10(7)	-6(8)	-220(9)
C(4)	520(10)	439(10)	554(13)	-41(9)	-22(9)	-175(9)
C(3a)	468(9)	439(10)	444(11)	-52(8)	-9(9)	-117(9)
C(3)	479(10)	522(12)	509(12)	-18(9)	-2(10)	-151(9)
C(2)	517(12)	615(13)	712(15)	77(10)	-21(12)	-238(11)
C(7)	570(13)	701(16)	853(20)	-90(12)	43(15)	-292(14)
C(8)	793(17)	446(11)	925(21)	-91(12)	7(13)	-377(16)
C(9)	457(10)	525(11)	588(13)	36(9)	-20(10)	-146(9)
C(10)	683(15)	605(14)	1221(24)	85(13)	50(15)	-397(15)
C(11)	674(16)	888(19)	1422(27)	220(16)	64(19)	-449(17)
C(12)	488(12)	1088(21)	959(20)	72(14)	-58(17)	-273(13)
C(13)	624(14)	837(18)	1158(23)	-96(14)	-83(17)	-334(15)
C(14)	614(13)	592(14)	1143(22)	19(11)	-73(14)	-383(14)

Table 2. Continued.

Atom	<i>U</i>	Atom	<i>U</i>
H(2)	69(8)	H(7,1)	108(9)
H(10)	119(10)	H(7,2)	78(6)
H(11)	135(10)	H(7,3)	91(8)
H(12)	102(7)	H(8,1)	121(9)
H(13)	113(9)	H(8,2)	85(8)
H(14)	99(8)	H(8,3)	82(7)

Table 3. Rigid body libration tensors L_1 and L_2 for various parts of the 3,4-dimethyl-6-phenyl-5,6-diaza-1,6a-dithiapentalene molecule.

Eigenvalues	Eigenvectors. Direction cosinus $\times 10^4$ relative to <i>a</i> , <i>b</i> , and <i>c</i> *, respectively			
L_1	19.1 ($^\circ$) ²	-9041	2141	-3698
	6.2	-1786	-9757	-1266
	5.5	-3883	-486	9203
L_2	118.9	-9665	-1547	-2047
	14.2	-2211	980	9703
	10.6	-1302	9831	-1289

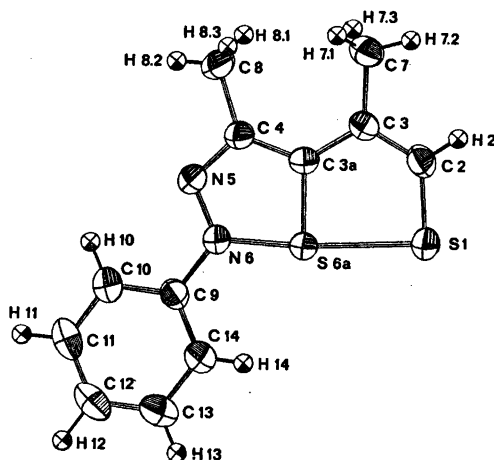


Fig. 1. The 3,4-dimethyl-6-phenyl-5,6-diaza-1,6a-dithiapentalene molecule with numbering of atoms. Thermal ellipsoids are shown. The thermal ellipsoids of the sulfur, nitrogen and carbon atoms enclose 50 % probability.

All the calculations mentioned above were carried out on the UNIVAC 1110 computer at the University of Bergen. The programs with a few exceptions, originate from the Weizmann Institute of Science, Rehovoth, Israel.

DISCUSSION

The molecular structure of the title compound with numbering of atoms is shown in Fig. 1.

The equation for the least squares plane through the atoms of the three rings with triple weight on sulfur is

$$-2.0930 x + 0.1246 y + 7.2047 z = 2.3164$$

where *x*, *y*, and *z* are fractional coordinates. Deviations from the plane are, S(1) -0.004, S(6a) 0.005, N(6) 0.016, C(2) -0.001, C(3) -0.006, C(3a) -0.007, C(4) -0.007, N(5) 0.005, C(7) 0.007, C(8) -0.045, C(9) 0.009, C(10) 0.008, C(11) -0.018, C(12) -0.013, C(13) -0.011, C(14) 0.013 Å. The methyl groups are eclipsed and the H(8,3)-H(7,1) and H(8,1)-H(7,3) distances are both 2.25(5) Å.

Table 4. Bond lengths *l* in 3,4-dimethyl-6-phenyl-5,6-diaza-1,6a-dithiapentalene. Standard deviations are given in parentheses. The l^I and l^{II} values have been corrected for libration according to the librational tensors L_1 and L_2 , respectively. The Δl values correspond to maximum corrections.

Bond	l (Å)	l^I (Å)	l^{II} (Å)	Δl (Å) $\times 10^3$
S(1)-S(6a)	2.487(1)	2.493		6
S(6a)-N(6)	1.774(2)	1.779		5
S(1)-C(2)	1.676(2)	1.681		5
S(6a)-C(3a)	1.737(2)	1.742		5
N(6)-N(5)	1.319(2)	1.324		5
C(2)-C(3)	1.366(2)	1.370		4
C(3)-C(3a)	1.416(2)	1.418		2
C(3a)-C(4)	1.412(2)	1.416		4
C(4)-N(5)	1.318(2)	1.321		3
C(3)-C(7)	1.509(3)	1.514		5
C(4)-C(8)	1.500(3)	1.505		5
N(6)-C(9)	1.411(2)	1.414	1.417	6
C(9)-C(10)	1.373(3)		1.397	24
C(10)-C(11)	1.378(3)		1.383	5
C(11)-C(12)	1.361(4)		1.381	20
C(12)-C(13)	1.354(4)		1.378	24
C(13)-C(14)	1.383(3)		1.388	5
C(14)-C(9)	1.373(3)		1.393	20

Table 5. Bond angles $\angle (ijk)$ in 3,4-dimethyl-6-phenyl-5,6-diaza-1,6a-dithiapentalene. Standard deviations are given in parentheses.

i	j	k	$\angle (ijk)^\circ$
C(2)	S(1)	S(6a)	88.9(1)
S(1)	S(6a)	N(6)	174.4(1)
S(1)	S(6a)	C(3a)	87.9(1)
C(3a)	S(6a)	N(6)	86.5(1)
S(6a)	N(6)	C(9)	123.7(1)
S(6a)	N(6)	N(5)	116.7(1)
N(5)	N(6)	C(9)	120.0(2)
N(6)	N(5)	C(4)	110.5(2)
N(5)	C(4)	C(8)	115.8(2)
N(5)	C(4)	C(3a)	116.3(2)
C(8)	C(4)	C(3a)	127.9(2)
C(4)	C(3a)	S(6a)	110.4(2)
C(4)	C(3a)	C(3)	128.8(2)
S(6a)	C(3a)	C(3)	120.8(2)
C(3a)	C(3)	C(7)	122.5(2)
C(3a)	C(3)	C(2)	118.5(2)
C(7)	C(3)	C(2)	119.0(2)
C(3)	C(2)	S(1)	123.9(2)
N(6)	C(9)	C(10)	120.4(2)
N(6)	C(9)	C(14)	120.1(2)
C(9)	C(10)	C(11)	119.2(2)
C(10)	C(11)	C(12)	121.5(2)
C(11)	C(12)	C(13)	119.2(2)
C(12)	C(13)	C(14)	120.5(2)
C(13)	C(14)	C(9)	120.1(2)
C(14)	C(9)	C(10)	119.5(2)

Bond lengths and angles with standard deviations, calculated from the values in Table 1, are listed in Tables 4 and 5, respectively. We

realize that the standard deviations probably should be multiplied by a factor of two to give a more realistic estimate.¹³

The bond lengths between non-hydrogen atoms have been corrected for libration,¹⁴ the l^I and l^{II} values in Table 4 are corrected according to the libration tensors L_1 and L_2 , respectively. The l^I values are chosen to represent the dimensions of the two fused rings as well as the lengths of the C(3)–C(7) and C(4)–C(8) bonds. For the dimensions of the phenyl group the l^{II} values are supposed to be the more reliable ones. The difference between these and the corresponding l^I values are due to the fact that the phenyl group has some individual libration relative to the other parts of the molecule, *cf.* Table 2. Attention should be drawn to column Δl of Table 4 where the values for C(9)–C(10), C(11)–C(12), C(12)–C(13), and C(14)–C(9) show the degree to which the individual libration of the phenyl group has affected the “observed” bond lengths.

The lengths of the S–C, C–C, N–N, and N–C bonds in the present structure (III) agree with those of the corresponding bonds in the 2-*t*-butyl-derivative (IV).¹ The length of the S–S bond, however, is significantly different in the two structures and so is the length of the S–N bond. This shows that substituents do affect the bonding in the S–S–N sequence of I.

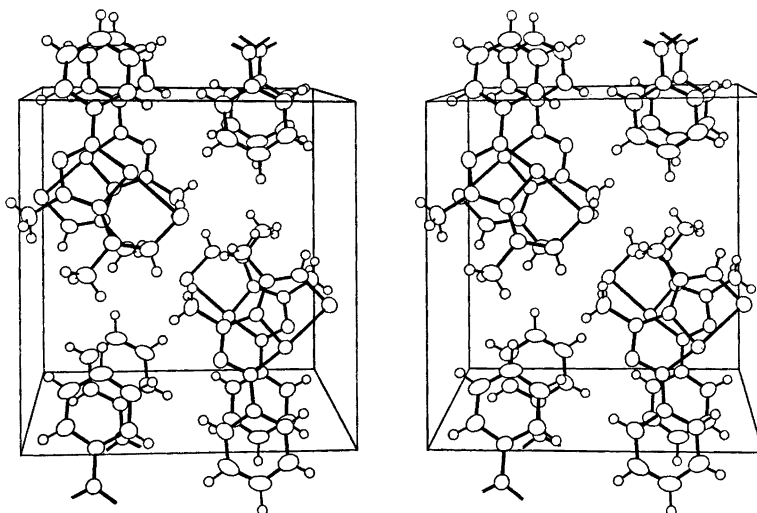
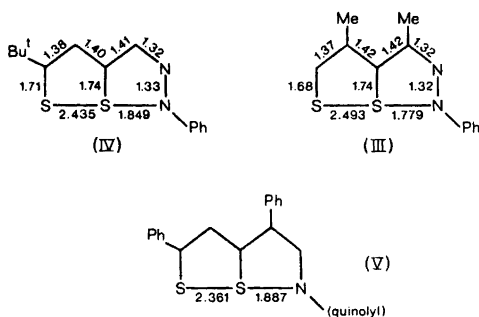


Fig. 2. Stereoview of the molecular packing.



The sums of the S-S and the S-N bond lengths in III, 4.272 Å, and in IV, 4.284 Å, are almost equal and close to the value 4.248 Å for the sum of the corresponding bond lengths in V.¹⁵ The S-N bond in the present structure, 1.779(2) Å, is only 1.7 % greater than the sum of the covalent radii for sulfur and nitrogen, 1.75 Å.^{16,17}

A stereoscopic view¹⁸ of the molecular packing in the unit cell is given in Fig. 2. There are no intermolecular contacts shorter than corresponding van der Waals distances.

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